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XVIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON A NEW METHOD OF DETERMINING GAS DENSITIES.

By Josiah Parsons Cooke.

Presented June 12, 1889.

In the well known method employed by Regnault for determining the density or specific gravity of air, oxygen, nitrogen, hydrogen, and carbonic acid, we deal primarily with tares, of which the weights to be determined are the differences. The glass balloon which holds the gas is tared by a similar balloon of exactly the same volume and of nearly equal weight, suspended from the opposite pan of the balance. The small difference of weight required to establish perfect equilibrium is alone measured with standard brass or platinum weights. Whatever may be the form of the subsequent calculation, the primary object is to obtain the tare of the empty balloon when absolutely vacuous. This known, the differences between such tare and the tare of the balloon filled with various aeriform substances, gives the weights of equal volumes of these substances under the temperatures and pressures at which the balloon was filled. The volume of the counterpoise is exactly adjusted to that of the balloon by the aid of a small subsidiary glass bulb (Plate II.); and by sealing up more or less mercury in this bulb it is easy to make the difference of weight such that the standard weights required to complete the equilibrium will measure the differences of tare to be determined, and no more.

In the method of Regnault the tare of the empty balloon, or what was equivalent to it, was found by exhausting the balloon with an air-pump and weighing it after measuring the tension of the residual gas while the glass was surrounded by ice. But it has been shown by Agamennone * and Lord Rayleigh † that the results thus obtained are

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* Atti (Rendiconti) d. R. Accad. dei Lincei, 1885.

† Proceedings of the Royal Society, vol. xliii. p. 362. 1888.

vitiated to a small extent by the circumstance that when the balloon is exhausted the pressure of the atmosphere determines a slight shrinkage of the external volume, which naturally disturbs the exactness of the compensation between the buoyancy of the air on the balloon and on its counterpoise. Although this shrinkage can be readily measured, as was done by Dr. T. W. Richards under my direction,* and still more recently by Professor Crafts,† who experimented on the balloon used by Regnault, which fortunately has been preserved, it seemed desirable to develop a method by which this correction could be avoided. For even if the new method should lead to no more accurate results than before obtained, it might serve to confirm the validity of the correction in question, and at least would give additional data towards establishing the value of important physical constants.

The new method we have devised for the purpose consists in first taring the balloon when filled with carbonic acid gas, and then drawing the gas through absorption tubes and determining its weight, as in the well known method of organic analysis. This weight known, the tare of the empty balloon is obviously the difference between the first tare and the weight in question. The practical problem here presented is, however, far more difficult than that of organic analysis. In the last, we expect to determine the weight of only a few decigrams of carbonic acid within a few tenths of a milligram, while in the problem now before us we must weigh at least nine or ten grams of carbonic acid, not simply to a proportional, but to an equal, degree of accuracy. We only succeeded in securing such accuracy after many trials and a careful study of all the conditions involved, and our primary object in this paper will be to describe the precautions which are essential to the success of the new experimental method. Incidentally it will appear that our results confirm in a most striking manner the high value of the specific gravity of hydrogen found by Lord Rayleigh,‡ and the low value of the atomic weight of oxygen found by ourselves.

The Balance and Weights.

The balance and weights were the same as those used by us in our previous work.§ The disposition of the apparatus which, after many trials, we have found most suitable for accurate work, is shown in

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* These Proceedings, vol. xxiii. p. 177. 1888.

† Comptes Rendus, vol. cvi. p. 1662. 1888.

‡ Proceedings of the Royal Society, vol. xlv. p. 426. 1889.

§ These Proceedings, vol. xxiii. p. 159. 1888.

Plate II. The balance rests on the plank shelf of a wooden case, whose glazed doors are shown open in the drawing; and as this shelf is firmly secured to a thick brick partition wall behind, great steadiness is secured for the instrument. Around the inside of the wooden case are hung folds of drapery, which surround the balance case and protect the beam from radiations, while a curtain rolling on a spring fixture enables the experimenter to uncover the front as necessary. Fastened by flanges and screws to the under side of the same shelf is a box made of tinned sheet iron, of somewhat larger dimensions than the balance case. The front of this box can be almost wholly uncovered by means of two large doors made of the same metal sheet, and secured when closed by turning buttons, but shown open in the drawing. In the metal top are two circular holes about half an inch in diameter, corresponding to holes through the shelf and the base of the balance case, and directly under the centres of the balance pans. From hooks soldered to the under side of the pans the globe and its counterpoise are suspended by means of brass wires, and the lengths of the wires are so adjusted that the two glass vessels shall hang midway in the metal box. The globe is hung from a wire stirrup, Plate I., which swings from an eye at the end of one wire; while on the neck of the counterpoise is cemented a brass cap and hook, and both it and the small subsidiary bulb are hung on an eye at the end of the other wire. Of course these details might be varied. It is only important that the whole system should swing freely, with as little friction as possible, and that the balloon should be easily removed and replaced.

Through a third hole in the top of the metal box and shelf, placed just in front of the balance case, passes a thermometer (not shown in the drawing) by which the temperature may be watched, and the inside of the box is painted with lamp-black so as to secure a uniform temperature throughout the interior. In our previous paper we spoke of the disturbance sometimes caused by currents of air within the box, but we found on further experience that these currents could be prevented by keeping the interior of the box as nearly as possible at the temperature of the external air. For this purpose it is important that the air of the room should circulate as freely as possible around the box, and the required condition is more easily secured if the box is made of thin metal sheet. It is also important that the temperature of the room should not be constantly changing, and that all circumstances should be avoided which would cause a flow of heat either into or out from the box. Sitting in front of the box in the process of weighing immediately causes a disturbance, and hence the division of the outer wooden case below the shelf is provided with wooden doors, which should be shut in front of the metal box before approaching the balance. When the thermometer hanging with its bulb inside the box indicates the same temperature as one hanging from the balance case outside within one tenth of a centigrade degree, the conditions are most favorable for accurate weighing.

In order to maintain the atmosphere within the box in a constant hygrometric condition, we placed in it four large open dishes of sulphuric acid, two on the bottom of the box and two on a shelf near the top, as described in our previous paper. The acid was first boiled with a fraction of a gram of ammonic sulphate, to remove the last traces of nitrous fumes, and renewed as occasion required.

We have found that we can most accurately estimate slight differences of weight with a balance thus loaded by observing the amplitude of the first swing of the pointer when the pans are relieved. With the balances of Becker, after the beam has been set on its bearings by the usual cam motion, the pans are still supported by two delicate arms, which are held by a weighted lever against the under side of the pans, but which can be pressed down by pushing against the button shown in the drawing on the front of the balance case. Such a mechanical arrangement is peculiarly adapted to this method of weighing, as it relieves the pans suddenly and under the same conditions, so that the amplitude of the subsequent swing is an accurate measure of the difference of weight acting at the two ends of the balance beam; and in this case the inertia of the heavy load renders the effects surprisingly uniform. We give these details, not because they involve any new principles, but because the results have been reached after a long series of experiments, and our experience may save others much loss of time. With the apparatus arranged as we have described it, a difference of weight amounting only to one tenth of a milligram was distinctly indicated, although the load exceeded half a kilogram on each pan, and the compensation was made so perfect that the equilibrium was not perceptibly altered by any ordinary changes of atmospheric conditions.

In order to reach such compensation, a counterpoise is first selected which on rough measurement appears to be nearly of the same volume as the balloon, and at the same time a little lighter in weight. The apparatus is then mounted with this counterpoise as described, the stopcocks of the balloon being closed. A series of observations are then made of the variations of weight arising from changes of atmospheric pressure and temperature, as carefully measured as possible. From such observations we can readily calculate, by the method we have previously described in these Proceedings,* the volume of the small bulb required to make the compensation perfect, and an experienced glass-blower can readily make a bulb of the size indicated, which, before it is sealed, may be adjusted as to weight by loading with mercury as above described.

The weights used in connection with the balance had been adjusted for our previous work with the greatest care, and not only compared with each other, but also compared with a copy of the Washington standard. Although we shall deal in this paper solely with relative weights, yet the absolute values that may be deduced from our results must be correct far within the limits of the experimental errors of our own work. The sum of the weights required to measure the differences of tare never exceeded twelve grams, and of this small mass any possible difference between our copy and the Paris standard kilogram must be wholly inappreciable.

THE GLASS BALLOON.

We have used in this investigation the same glass balloon that was fitted up for a somewhat different purpose in our work on the atomic weight of oxygen, but which has proved equally well adapted to determinations of gas density. Regnault in his work on the same subject used a balloon of ten liters' capacity, having its neck closed with a brass cap and stop-cock, and filled it by alternately exhausting the interior with an air-pump and refilling from a gasometer until the complete purity of the enclosed gas was assured. After long experience with this mode of experimenting, we have found it more convenient to fill the balloon by displacement directly from the generator, and we have found that we can reach a satisfactory result with least labor in this way.

Our balloon is represented in Plate I., which shows all the details of its construction. It was made by Emil Greiner of New York, and all the joints are so finely ground that when properly lubricated they will hold a vacuum indefinitely. The peculiar form of the stop-cocks enables the experimenter to shut into the globe a definite volume of gas and at the same time open a vent to the generator through the side tube; or to allow the gas to flow through the side tube until the current is perfectly pure before it is admitted to the balloon; and again, when the stop-cocks are both closed and the balloon disconnected, all the gas left in the connecting tubes will soon be replaced by air. At the freezing point the internal volume of the balloon, as nearly as we have been able to measure it, is 4961.5 cubic centimeters, and the weight of the glass 570.5 grams. After much experimenting, we have concluded that as great accuracy in determinations of gas density can be obtained with a balloon of this size as with a larger one. The advantage to be derived from the greater mass of gas experimented on is more than compensated by the greater liability to error which the weighing of larger vessels and the longer duration of all the processes involve.

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* Vol. xviii. p. 55.

The extent to which this balloon is actually compressed by the tension of the atmosphere when a vacuum is made in the interior has been carefully measured,* and amounts to 1.66 cubic centimeters for a difference of tension of 760 mm. between the interior and exterior of the glass vessel; and this corresponds to a loss of buoyancy of 1.96 milligrams in the air at 760 mm. and 22° C.

When the balloon was not hanging on the balance, it was always protected by a metal case (see Plate II.), from which the neck and connecting tubes alone protruded, and in transferring the balloon to and from the balance it was handled only by the neck.

In Regnault's experiments the balloon was filled with the gas under examination at the temperature of 0° C. by surrounding the glass with melting ice. This necessitates a careful cleaning of the globe at least twice during each determination, and thus may arise slight variations of condition to impair the accuracy of the results. We have found with Lord Rayleigh that it is preferable to fill the balloon at the temperature of the laboratory, but we must then observe the temperature with very great accuracy. It is important to know the temperature to the one hundredth of a centigrade degree, for even so small a difference of temperature as this causes a change in the amount of carbonic acid gas which our balloon will hold under ordinary atmospheric conditions corresponding to three tenths of a milligram.

We have found it possible to secure even such constancy of temperature as this delicate measure implies by placing the balloon while filling in a calorimeter case, and observing the temperature with a calorimetric thermometer divided to the fiftieth of a centigrade degree. The calorimeter case consists of a cylindrical vessel of sheet zinc wide enough to receive the balloon with its tube and leave a play of less than an inch on either side. This vessel is fastened by metal stays inside a second cylindrical vessel of the same material, leaving an annular space about two inches wide and an equal space between the bottoms of the two vessels, all of which is filled with water. In addition, the water vessel is further protected by a layer of felt one inch thick kept in place by an outer covering of the same sheet metal. When in use, the top is covered by a cap made also of thick felting, and in the crown of the cap is a slit, through which a thermometer may be inserted or the hand passed to turn the stop-cocks. The gas to be used is conducted into the calorimeter through a very small lead tube, which is connected with the lower tubulature of the stop-cock by a rubber connection, and the balloon is so placed that the current shall enter either at the top or at the bottom of the vessel, according as the gas is lighter or heavier than the atmosphere. The calorimeter case stands about four feet high, and the balloon rests in it on a down cushion, with the connecting tubes fully six inches below the surface of the water in the annular space above mentioned. With this apparatus it was possible to keep the temperature of the balloon constant within the one hundredth of a centigrade degree for an hour at a time, unless the temperature of the laboratory suddenly and greatly changed.

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* These Proceedings, vol. xxiii. p. 182.

The general arrangement for filling the balloon was then as follows. The gas delivered from the drying tubes of one of the generators hereafter to be described passed through the lead tube of which we have spoken to one or the other, as the case might be, of the tubulatures of the balloon standing in the calorimeter. Passing out by the opposite tubulature, the current was conducted by a similar lead tube to a second but much larger balloon serving as a gasometer, and from the last vessel through a gas wash-bottle to the atmosphere. The bottom of the wash-bottle was covered with strong sulphuric acid to dry any returning air, but not deep enough for the inlet tube to dip under the liquid. The current was continued until the proper test showed that the gas issuing from the end of the apparatus was perfectly pure. Then the inlet cock of the balloon was turned, and the temperature of the calorimeter case watched until constant, and a sufficient time had elapsed to establish a perfect equilibrium with the atmosphere through the connecting tubes and vessels. This, as we found by experience, often requires longer time than we were led to anticipate, and when experimenting with carbonic acid gas it is not safe to allow less than twenty or thirty minutes; and now the large balloon and wash-bottle come into play to prevent air diffusing into the balloon, or being drawn back in consequence of changing pressure.

When all the conditions seemed to be satisfactory, the temperature of the calorimeter and the height of the barometer were accurately observed, the first to the hundredth of a centigrade degree and the last to the twentieth of a millimeter, noting always the height of the attached thermometer. The hand was then quickly thrust into the calorimeter, and the outlet cock at once closed. The balloon was now removed, dusted with a large camel's-hair brush, and hung in its place on the balance. When, however, the atmosphere is very dry, as it often is in this climate during the winter months, it may happen that the surface of the glass acquires a charge of electricity from the friction of the cushion in the calorimeter or of the brush just mentioned; and if there is any suspicion of such an effect, the best way to dissipate the charge is to stand the balloon for a few minutes in its metal case (shown in Plate III.), after covering the bottom of the case with a thin layer of water. If the balloon is hung on the balance with a charge of electricity on its surface, however small, it will be unequally attracted by the surrounding metallic walls, and most confusing anomalies ot weight will be noticed. Moreover, in the very dry atmosphere of the case the charge will last for days, or even weeks, as on the insulated vanes of an electrometer.

THERMOMETERS AND BAROMETERS, AND THEIR CORRECTION.

The thermometers on whose indications we have relied in this investigation are two of small range, but divided into fiftieths of a centigrade degree and made by the house of the late Dr. H. Geissler of Bonn. We were obliged to use the two, for our investigation was continued into summer weather, which exceeded the range of the thermometer first selected. As should always be the case with such instruments, the zero point is given in each case on a short subsidiary scale, separated from the main scale by an enlargement of the tube. Careful observation showed that the zero point of the instrument we will designate as No. 1, was depressed 0.02 of a centigrade degree, while the zero point of No. 2 was raised 0.28 of a degree. Making the correction thus indicated, to be added to all temperatures observed with No. 1, and subtracted from all observed with No. 2, the two instruments were found to agree exactly through all portions of the scale common to both. Obviously, therefore, the differences of temperature observed are perfectly trustworthy to the one hundredth of a degree, but how far the absolute values — counting from the freezing point of water — can be relied on when compared with the observations of other experimenters, we have no means of determining. Of course, it will be understood that all temperatures hereafter given have been corrected for the variation of the zero point. At the close of the investigation the zero points were again tested and found to be unchanged.

The barometer used was a large standard instrument of the familiar mountain form, made by Greene of New York. Hanging at the side of it was a smaller instrument of the same maker, whose indications agreed with the first within the tenth of a millimeter. Here again, as in the case of the thermometer, there can be no question as to the accuracy of the differences of tension observed within moderate limits; but how far the absolute heights can be compared with those observed by Regnault and others is also a problem that cannot be readily solved, and one not within the means of a single experimenter to determine. All heights of barometer given hereafter have been reduced to 0° by the tables of Guyot.*

TARE OF THE EMPTY BALLOON BY REGNAULT'S METHOD.

In the method of experimenting devised by Regnault the tare of the empty glass globe used, although not explicitly given, was implicitly determined. His arrangement for filling the globe, shown by Figure 1, has already been referred to, and his general method of experimenting consisted in taking the tare of the globe when filled with the same gas at the temperature of melting ice under as different tensions as possible. The tensions were found by measuring with a cathetometer the difference of height, $\alpha\ \beta$ (see Fig. 1), under each condition, and the tares were found by means of the balance by the system of compensation already described. The difference of tare gives the weight of gas which the globe contains at 0° at the tension $H - h$, and from this may readily be deduced the weight at any other tension; as, for example, at the standard tension of 760 mm. The calculated weight at either of the tensions H or h, deducted from the corresponding tare, gives what we have called the tare of the empty globe; but obviously with Regnault's method this value is not needed in the calculations of specific gravity or density.

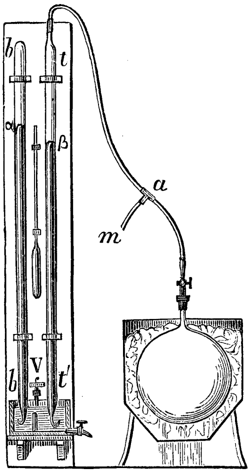

FIG. 1.

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* Published by the Smithsonian Institution, Washington.

When the globe is filled by displacement it conduces to greater accuracy to determine independently the tare in question; and as soon as the details of the new method had been worked out, we began our final determinations by taking according to the old method the tare of the balloon above described when empty, so as to obtain a definite standard of comparison for further results. We however varied the method of Regnault in so far that we always filled the globe with hydrogen before exhausting the interior. As with this exceedingly light material the weight of the residual gas seldom exceeded one half a milligram, an error as great as one fifth in the capacity of the balloon or in the tension of the residual gas would cause no appreciable difference in the value of the small weight we sought to estimate. The details of a single example will be sufficient to illustrate the procedure.

DETERMINATION No. 1.

A current of hydrogen gas from the electrolytic generator described in our previous paper* was run through the balloon from Saturday, May 25th, at 4 o'clock P. M., to Monday, May 29th, at 10 o'clock A. M., 1889, the balloon standing in calorimeter case connected with larger balloon to receive overflow. At moment of closing, the height of barometer and temperature of the case were observed, but these data are not required for the present determination, and will be given hereafter when used for calculating the specific gravity of hydrogen. The balloon was exhausted with an excellent mechanical air-pump,† and the tension of the residual gas measured by means of a siphon manometer interposed between the balloon and the pump. The form of manometer used is shown by Figure 2. It was made in the laboratory, and in filling it with mercury the liquid metal, purified by repeated distillation, was boiled in the tube with the greatest care. For convenience, the difference of level of the mercury in the two arms was measured with a cathetometer constructed by the Société Genevoise, but it might have been estimated with sufficient accuracy by the millimeter scale of the instrument. Tension in balloon after exhaustion 456.95 — 455.55 = 1.40 mm.

Assuming 0.4164 as the approximate value of the weight of hydrogen gas filling the balloon at 763.10 mm. and 21°.08 C. (p. 227), the weight of the residual gas at 1.4 mm. and same temperature would be

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* These Proceedings, vol. xxiii. p. 168.

† Author's Chemical Physics, p. 331.

0.00076 gram or 0.76 m.g. No exact observation of the temperature of the balloon was necessary; for a difference of 4° C. would not alter the above value more than $\frac{1}{100}$ m.g., and we may therefore assume that the temperature of the balloon was the same as that of the laboratory, which at the time was 21° C. The correction for lessened buoyancy (increased weight) on account of the contraction of the balloon by atmospheric pressure amounts, as has been shown, to 1.98 m.g.,* and this added to 0.76 makes the total correction 2.74 m.g. When the balloon was hung on the balance, the weight required to complete the tare was 2.5600 grams. Hence we have, —

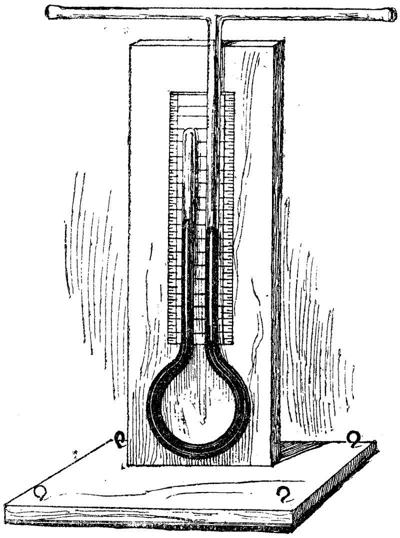

Fig. 2.

Weight of balloon exhausted		2.5600 grams.
Correction for residual gas . . .	0.76 m.g.	
" " lessened buoyancy .	1.98 "	27 "
Tare of empty balloon		2.5573 "

Two other determinations were made in the same way, and the three results are united in the following table.

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* These Proceedings, vol. xxiii. p. 184.

Summary.

Tare of empty balloon, 1st value	2.5573	grams.
" " " 2d "	2.5572	"
" " " 3d "	2.5574	"
Mean value, ...	2.5573	"

TARE OF THE EMPTY BALLOON BY CHEMICAL METHOD.

The general theory of this method has already been stated. The balloon is filled with carbonic acid gas by displacement, and the tare taken. The gas is then drawn through a series of absorption tubes, as in the process of organic analysis, and the sum of the increased weights of these tubes gives the weight of the total contents of the balloon at the time the tare was taken. The weight of the balloon filled with carbonic acid gas less the weight of the carbonic acid thus determined is obviously the tare of the empty balloon required. In attempting to perfect this apparently simple experimental method we met with unexpected difficulties, arising from several circumstances.

In the first place, in order to wash out from the balloon the last traces of carbonic acid, it was necessary to draw through the apparatus a very large volume of air, and the system of purifiers and desiccators needed absolutely to free the atmospheric air from the least admixture of carbonic acid or aqueous vapor was found to be far more extensive than we anticipated. In the second place, since the globe held, at the ordinary temperature of the laboratory and at the average pressure of the atmosphere, no less than nine grams of gas, the common potash bulbs used in organic analysis were wholly inadequate for our requirements, and we only succeeded after many trials in finding a form of apparatus by which so great an amount of carbonic acid could be determined with the necessary accuracy, that is, within a few tenths of a milligram. The arrangement finally adopted is shown in Plate III. The balloon is represented standing in its covered metallic case, in which it is placed the moment it is taken from the balance. On the right of the balloon and below it is a system of tubes for purifying and drying the atmospheric air which enters from outside the laboratory by the flexible tube on the extreme right. On the left of the globe is a system of tubes for absorbing the carbonic acid. The flexible tube on the left is connected with a Bunsen pump through a form of Mariotte's flask,* and by this means a current is maintained through the whole system, under constant pressure.

PURIFYING AND DRYING APPARATUS.

The air entering as we have described passed first through a wash-bottle of familiar construction containing a solution of potassic hydrate, Sp. Gr. = 1.44, and then through a similar wash-bottle containing a concentrated solution of baric hydrate; and if the rapidity of the current was not greater than two bubbles a second, this double washing was found sufficient to remove the last traces of carbonic acid. Indeed, as soon as the baryta water showed the least indications of cloudiness, the solutions were renewed. It was not so easy to remove the last traces of moisture.

After the air had passed the washing flasks it entered a system of desiccators, shown in the lower half of the plate, where in small bubbles it travelled up first one tube, and then a second tube, both 5½ feet long, and filled with concentrated sulphuric acid previously boiled with a small amount of ammonic sulphate to remove all nitrous fumes. Leaving the second of these tubes it entered an elongated bulb four inches long by two inches in diameter filled with phosphoric anhydride; and the fact that prolonged contact with sulphuric acid is not sufficient to remove the last traces of moisture was shown by the circumstance that after the current has passed for several days the dry white powder at the opening of the bulb showed signs of deliquescence.

Our phosphoric anhydride was prepared by burning common yellow phosphorus in a large sheet iron drum, through which a current of dry air was drawn with sufficient rapidity to maintain the phosphorus in rapid combustion, and the bottom of the drum was made tunnel-shaped so that the anhydride could be shaken down into a self-sealing fruit jar as fast as it formed. As thus prepared the anhydride has a slight odor, which it loses after a prolonged current of dry air has been drawn through the powder; and after our drying tubes had been filled their contents were submitted to a preliminary treatment of this sort, and not until long after all perceptible odor had disappeared were they used in our work. We noticed that after the anhydride had been used for some time it appeared more granular and lost in part its hygroscopic power. In order to make sure of this point, the apparatus as far as described having been in use for several weeks, we connected with the first phosphoric anhydride tube a weighed tube containing fresh anhydride. After drawing air through the system at the same rate and during the same time as in a carbonic acid determination, we reweighed this second tube and found that it had gained 5.5 m.g. We next added to our system the U tube filled with phosphoric anhydride, which is shown in Plate III. immediately before the balloon, and repeated the experiment. There was then no gain in weight perceptible. The observations were as follows.

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* These Proceedings, vol. xxiii. p. 163.

Before interposing the U Tube.

		H	T°	R
1st weight P_2O_5 tube	25.9212 grams	295.7	20.0	302.7
2d " "	25.9267 "	295.2	20.8	301.4
	0.0055 "			1.4

After interposing the U Tube.

		H	T°	R
1st weight P_2O_5 tube	25.9268 grams	299.3	19.6	306.7
2d " "	25.9268 "	299.2	21.6	304.6
				2.1

In this table the column headed H contains the barometric pressure at time of weighing in tenths of an inch; that headed T° gives the corresponding temperatures of the balance case in centigrade degrees. By adding to the values H the quantities $(27 - T)^\circ$ we obtain the values R, and these are the barometric heights which would give an atmosphere of the same density, and therefore exerting the same buoyancy, as the atmosphere at the time of weighing if the temperature were uniformly 27° C. The correction that should be made for differences of temperature and pressure at successive weighings can at once be calculated from these values. We found by experiment that for the phosphoric anhydride tube used in these and in subsequent determinations the correction amounted to 0.04 m.g. for each tenth of an inch change of pressure, and hence in the above weighings the correction is too small to be appreciable. This simple method of correcting weights for changes in the buoyancy of the atmosphere has been described in a previous paper in these Proceedings.* In order to apply it readily, the barometric heights, although usually read in millimeters, were often also notéd, as here, in tenths of inches, and the instrument we used was provided with both scales.

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* Vol. xviii p. 55.

It is obvious from the above experiments that the hygroscopic power of phosphoric anhydride becomes impaired before the powder actually deliquesces, and we have dwelt on the point because the experience was of great importance in our investigation by leading us to add the second anhydride tube to our system, and also to watch carefully the condition of its contents and to replace the tube as soon as the least change was perceptible. We attribute the change to a glazing of the amorphous grains due to the forming of a coating of glacial phosphoric acid, but the effect is one that would not be noticed except under such extreme conditions as existed in our work. We now pass to the system of absorption tubes on the other side of the balloon.

Absorption Apparatus.

The apparatus for the absorption of the carbonic acid gas must meet very opposite requisitions. In the first place, it must offer a sufficiently large mass of absorbent to the pure gas which first comes to prevent overheating from the rapid chemical combination. In the next place, it must be capable of removing the last traces of carbonic acid from the air which is afterwards drawn through the tubes. Lastly, it must not be so heavy or so complicated that it cannot be promptly and sharply weighed, and the correction for changes of temperature and pressure between successive weighings accurately estimated.

After trying in various ways to enlarge and modify the different forms of potash bulbs and spiral tubes in general use, (and in these attempts we had the aid of a skilful glass-blower,) we found that we could reach a more accurate result with a system of separate tubes, in spite of the number of weighings they involved. To absorb the great mass of the carbonic acid we used the simplest form of gas washer, shown in Plate III. at A. The bulb had a capacity of 200 c.c., and in this we placed 75 c.c. of a solution of potassic hydrate having Sp. Gr. = 1.443. When empty the bulb weighed only 57 grams, and when filled about 165 grams. Assuming that the potash was fully neutralized, less than one half of this amount would be sufficient to combine with nine grams of carbonic acid; but to insure prompt action and avoid excessive heating the amount given is required.

The potash tube was followed by a small U tube, four inches long, with ground caps filled with finely granulated soda lime, and weighing when full about 40 grams. (See B, Plate III.) To this was united a similar U tube containing phosphoric anhydride to hold the aqueous vapor, which is brought over by the gas current in no inconsiderable amount from the potash solution and the soda lime, in consequence of the heat set free by the absorption. The anhydride tube weighed when full about 25 grams, and is shown at C. Next was a third U tube filled with glass beads and having a few drops of strong sulphuric acid at the bend. This tube, D, was not weighed, but was necessary in order to indicate any sucking back of the air and to prevent any vapor from thus reaching the phosphoric anhydride. The double bulb forming the end of the system, shown at E, was made by melting together the usual inlet tubes of two gas washers like A. In this we placed 50 c.c. of a standard solution of baric hydrate, and the peculiar construction was necessary in order to provide against regurgitration in consequence of back pressure. The solution is easily washed out of the bulbs, and when retitrated at the end of the process gives the amount of carbonic acid, if any, which escaped the other absorbents. All of these tubes were united into one system by rubber connections carefully lubricated both inside and out with vaseline, a soft paraffine which had previously been melted and heated to remove every trace of moisture.

The manipulation of this apparatus was an interesting experiment. When all had been set up as shown in Plate III., the globe being full of carbonic acid, the Bunsen pump was first started, and after a constant suction (regulated by the Mariotte's flask before described) had been established, we cautiously opened the cock of the balloon, which connected with the potash bulb, closely watching the flow of gas. As soon as this flow began to slacken, we as cautiously opened the farther cock, by which air was admitted to the balloon through the line of purifiers, still closely watching and regulating the flow. We then noticed a striking phenomenon. As pure carbonic acid was now passing into the potash bulb, the air mixing but slowly with the heavy gas at the surface of contact as the level sunk in the balloon, the absorption at first was complete. If the air supply from behind was not sufficient, a partial vacuum formed in A, and air was drawn back through the tubes in front, as indicated at once by the bubbles at the bend of D; but if the supply was carefully regulated, a perfect equilibrium could be maintained in the tubes beyond, and we have seen the carbonic acid flow into the potash bulb for half an hour without more than a few bubbles of air passing through the sulphuric acid at the bend of D in either direction.

After a while, however, when the great mass of the carbonic acid has been absorbed, bubbles of air begin to pass through D, and also bubble through the baryta water beyond, and soon a steady current is established throughout the whole apparatus, which may then be left to take care of itself. If the current does not exceed in rapidity two bubbles a second, it may be allowed to flow for twenty-four hours without risk, and in that time every trace of carbonic acid will have been washed out of the balloon. The suction should now be stopped, and the cocks of the balloon closed. The tubes A, B, and C may then be disconnected, and after they have come to equilibrium in the balance case reweighed. The double bulb E must also be disconnected, the baryta washed out into a suitable bottle, and the solution retitrated with oxalic acid.

As the weights of the tubes A, B, and C must be corrected for the buoyancy of the air, it is essential to note the temperature of the balance case and the height of the barometer at the time of each weighing. The corrections in question may be considered under two heads; first, that made necessary by a change of temperature or pressure between successive weighings; secondly, that required to eliminate the effect of atmospheric buoyancy on the total weight of carbonic acid absorbed.

The first correction is best made by the method already described, and the application of this method was greatly facilitated in the present investigation by the circumstance that the same tubes, with the same weights of contents, were used in all the carbonic acid determinations made. We were able to determine once for all for each tube the correction required for a variation of one tenth of an inch in the barometric height reduced to 27° C.,* and then the correction in any case could be found by a simple multiplication. Thus we estimated that the correction for one tenth of an inch in the barometric height reduced to 27° C. was, —

For the potash bulb before absorption, . . .	0.306 milligram.
" " " after " . . .	0.321 "
" soda lime tube	0.067 "
" phosphoric anhydride tube	0.040 "

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* That is, reduced to the height which would be required to give at the temperature of 27°, an atmosphere of the same density and buoyancy as that at the temperature of the balance case when the tube was weighed. These Proceedings, vol. xix. p. 55.

Calculation of Correction for Potash Bulb.

	Before Absorption.	After Absorption.
Weight of glass	57.45 grams.	57.45 grams.
Volume of glass = 57.45 ÷ 2.5	23 c. c.	23 c. c.
" KOH solution	75 "	80 "
	98	103
" brass weights, 164 ÷ 8.2	20 "	
" " " 173 ÷ 8.2		21 "
Uncompensated volume	78 "	82 "
Air displaced at 27° C. and 300 tenths of an inch.		
1.176 × 78	91.928 m. g.	
1.176 × 82		96.332 m. g.
Variation for $\frac{1}{300}$	0.306 "	0.321 "

The correction of the total weight of carbonic acid for the buoyancy of the atmosphere was not so simple a problem; but by using the same bulb and nearly the same volume of the same solution of potassic hydrate in every case, it was sensibly the same for all the determinations. The specific gravity of the solution of potassic hydrate before the absorption was 1.443, and tested in two separate determinations after absorption it was found to be 1.464 in each case. Using now the arithmetical means of the weights of the potash bulb in the three determinations under consideration, it was easy to find an average value for the correction thus.

Average weight of potash bulb before absorption	165.02 gr.
Weight of glass	57.45 "
" solution of KOH	107.57 "
Volume of solution of KOH = 107.57 ÷ 1.443	74.55 c. c.
Average weight of potash bulb after absorption	173.57 gr.
Weight of glass	57.45 "
	116.12 "
Volume of solution of KOH = 116.12 ÷ 1.464	79.32 c. c.
Difference of volume = 79.32 – 74.55	4.77 "
Weight of CO_2 absorbed in potash bulb = 173.57 – 165.02	8.55 gr.

Volume of brass weights = 8.55 ÷ 8.2 . . . . . 1.04 c. c.
Uncompensated volume = 4.77 — 1.04 . . . . . 3.73 "
Weight of 3.73 c. c. of air at 300 tenths inch and
27° C. = 1.176 × 3.73 = corr. required . . 4.39 m. g.

In this calculation we have necessarily left out of the account both the small amount of carbonic acid absorbed by the soda lime and the water carried by the current from the potash bulb to the connecting tubes; for the increased weight of these tubes results from both these causes, whose relative effects or whose influence on the correction we cannot estimate. That they would tend to raise slightly the value of the correction is obvious; and if we assume, as we have in the following calculations, that the value is 4.5 milligrams we shall approximate as nearly to the precise amount as circumstances will permit. For all these corrections the data are only known within certain narrow limits; but the total uncertainty thus arising does not exceed two or three tenths of a milligram in the final result.

In weighing the potash bulb and U tubes it is of course essential that they should be left in the balance case until a perfect equilibrium of temperature has been reached, and then they must be weighed when open so that a perfect equilibrium of pressure on the inside and outside of the glass may be secured. And since we were here aiming at very great accuracy, we felt it important to inquire further whether any gain of weight from hygroscopic moisture was possible during the time necessary to verify the weight while the tubes remained open on the scale pan. We therefore carefully investigated this point. The air in the balance case was kept as dry as possible by an open dish of sulphuric acid, and the experiments were made under such conditions. It was found that the weight both of the potash bulb and of the soda lime tube remained absolutely constant, hour and hour together, except so far as they were influenced by changes of temperature and pressure, but the weight of the phosphoric anhydride tube slowly but uniformly increased at the rate of 0.025 m.g. per hour. We followed the change on one occasion from $10^{h.}$ $45^{m.}$ A. M. to $6^{h.}$ $15^{m.}$ P. M., and during these seven hours and a half the gain was 1.9 m.g., while the changes of temperature and pressure meanwhile were not enough to cause a sensible difference in the atmospheric buoyancy. Such experiments were continued for a sufficient length of time to enable us to confirm the values of the corrections above given, and they gave us great confidence in our weights. They showed that the only precaution necessary for accuracy was to close the tubes as soon as they were disconnected, and to leave each of them closed in the balance case until it was time to take the weight. The U-shaped tubes with perforated ground stoppers, by which connection with the lateral tubes can be instantly opened or closed, are admirably adapted to this work. As an example, we give next the details of one determination of carbonic acid by the method we have described.

Details of a Determination of Carbonic Acid.

The gas was generated from statuary marble and dilute hydrochloric acid in an apparatus precisely similar to that described and figured by us in a previous paper.* It was first washed by a solution of potassic bicarbonate, and then, having passed in succession over calcic chloride, sulphuric acid, and phosphoric anhydride, it was conducted into the balloon and overflow in the manner already described. The gas was tested by leading the current from the overflow into a familiar form of nitrogen apparatus filled with a solution of potassic

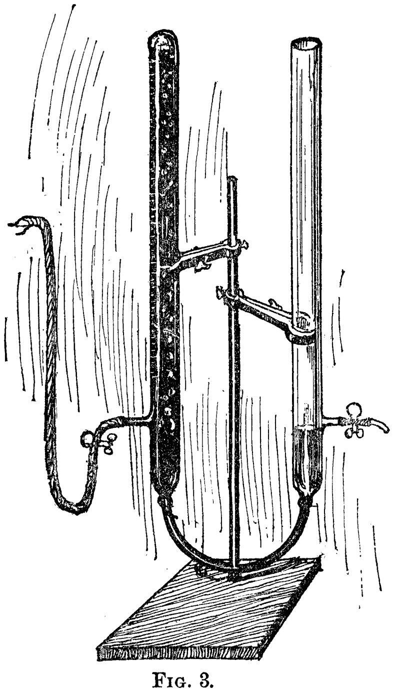

Fig. 3.

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* These Proceedings, vol. xxiii. p. 166.

hydrate (Fig. 3), and not until no measurable residue was left by a full liter of gas was its condition regarded as satisfactory. The balloon stood in the calorimeter case, and when the cocks were closed with the precautions already described the temperature of the case and the height of the barometer were observed, and although these values are not needed for determining the tare of the empty balloon, they will be used for determining the density of carbonic acid hereafter. The balloon was then disconnected and hung on the balance, and its tare found to be

$$W = 11.5907 \text{ grams.}$$

The balloon was then transferred to its metal case, and, having been mounted as shown in Plate III., the determination of the weight of its contents proceeded as just described.

Potash Bulb.

	Grams.	H	T°
1st weight of potash bulb	165.3388	299.99	25.8
2d " " "	174.0132	299.83	27.0
	8.6744		
Correction* for change of H and T	4		
	8.6740		

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* Since the volume and density of the potash solution used were closely the same in all the determinations, whether compared before or after the absorption, the value of the correction may be assumed to be the same in all cases, and, as has been shown at page 218, amounts to 0.306 m.g. before absorption and 0.321 m.g. after absorption for every change of one tenth of an inch pressure or 1° centigrade temperature from the standard of 300 tenths inch and 27° C. or 300° absolute temperature. The correct mode of calculating the correction in any case is to reduce both weights to what they would appear to be at $H = 300$ and $T_0° = 300 = 27°$ C. before taking their difference, using the value 0.306 for the smaller of the two, and 0.321 for the larger.

299.89 at 25°.8 corresponds in buoyancy to 301.09 at 27°
299.83 at 27° " " " 299.83 "

301.09 — 300 = 1.09 and 1.09 × 0.306 = 0.33 addative.
299.83 — 300 = —0.17 and —0.17 × 0.321 = —0.05 subtractive.

Then 165.3388 + 0.33 = 165.33913
174.0132 — 0.05 = 174.01315
8.67402 as before.

As regards the sign of the correction, notice that, when reduced to H = 300, the buoyancy becomes less and the *apparent* weight greater if the previous pressure was above 300, and *vice versa*.

Soda Lime Tube.

	Grams.	H	T°
1st weight of soda lime tube	42.8731	299.54	26.6
2d " " " "	43.1857	299.87	27.4
Correction insensible	0.3126		

Phosphoric Anhydride Tube.

1st weight of anhydride tube	39.5196	299.50	27.0
2d " " " "	39.5493	300.00	27.2
Correction insensible	0.0297		

Standard Solution of Baric Hydrate.

Before absorption, 50 c. c. required 46.60 c. c. solution of oxalic acid.
After " " " 43.65 " " "
2.95

One c. c. of decinormal solution of oxalic acid contains 0.0126 gram of $H_2C_2O_4 . 2\,H_2O$, corresponding to 0.0044 gram of CO_2.

$$2.95 \times 0.0044 = 0.0130 \text{ gram of } CO_2.$$

Total Weight of Carbonic Acid.

	Grams.
From potash bulb	8.6740
" soda lime tube	0.3126
" anhydride tube	0.0297
" titration	0.0130
	9.0293
Reduction to vacuum	45
	9.0338
Tare of balloon and gas	11.5907
Tare of empty balloon	2.5569
Value by Regnault's method	2.5573

The value of the tare of the empty balloon found by the new chemical method is directly comparable with that obtained by the Regnault method, since there was no change in the balloon meanwhile. But after this determination was finished, the balloon, as it remained standing in its case, having been exposed to the direct sunshine of an unusually hot June day, some of the cerate lubricating the stop-cocks melted and ran down into the tubulatures below, from which it had to be removed. Thus the tare was lessened by nearly a centigram. It was easy, however, to determine the exact loss, and as in a like investigation, even when using the greatest care, one must ever be liable to accidents of this sort, it is important to dwell on this point.

In losing the tare we had apparently lost the thread of our investigation, but we were readily able to recover this thread without interrupting the general course of the work. It must be borne in mind that our immediate object was to obtain by the chemical method a series of results for the tare of the empty globe which could be compared with the mean value 2.5573 obtained by the method of Regnault. Here had come a change of tare, and we could obviously find a new standard of comparison by redetermining the new value by the old method. But this was not necessary. In the first determination by the chemical method, we had observed with great precision the pressure and temperature at which the balloon was filled. We do the same in the second determination, to which we next proceed, although these values are not needed in this determination, by itself considered, any more than they were in the first. If now from the tare of balloon and gas in the first determination (11.5907) we deduct 2.5573, we have the weight of carbonic acid which the balloon contains at a known temperature and pressure as found by the method of Regnault. If we deduct the same quantity from the tare found in the second determination, we have the weight of gas which the balloon holds at another temperature and pressure by the same method. If now there has been no change of tare, these two weights ought to agree exactly when one is reduced to what it would have been under the conditions at which the other was taken; and if there has been a change of tare, the difference of the weights thus reduced will give the exact amount of the loss, on the basis solely, let it be noticed, of results obtained after the method of Regnault. Thus we have, —

			Grams.
By No. 1, weight of CO_2 at	763.85 mm.	and 25°.08	9.0273
" No. 2, " "	756.73 "	" 22°.40	9.0334
Weight No. 1 reduced at	" "	" "	9.0241
Loss of tare			9.3 m.g.

Obviously the accuracy of this result depends upon the accuracy with which the observations of temperature and pressure were made, and upon the correctness of the data on which the reductions are based. That the accuracy is extreme will appear from a comparison of the values of the specific gravity of carbonic acid, given on page 229, which were deduced from the same elements. And although in such work as this there is an obvious liability to error from just such a change of tare as we have been discussing, yet the loss or gain thus resulting is usually of such a magnitude that it cannot be overlooked.

Besides the one of which the details have been given, we made by the chemical method two other determinations of the tare of the empty globe in precisely the same manner as before described, and obtained the values 2.5481 and 2.5475 respectively. In order to bring these results into comparison with that obtained by the first determination, or those obtained by the method of Regnault, we must add 9.3 m. g. to each value. We then have for

Tare of Empty Balloon.

	Regnault's Method.	Chemical Method.
No. 1	2.5573	2.5569
No. 2	2.5572	2.5574
No. 3	2.5574	2.5568
Average	2.55730	2.55703

These results are essentially identical, and the two methods confirm each other. But having reached this important conclusion, which was the main object of our investigation, we freely concede the preference to Regnault's method. The difference between the results of the two methods, as here exhibited, is insignificant; but so long as the validity and value of the correction for the contraction of the balloon on exhaustion has been thus established, Regnault's method will be preferred because it is practically more simple, and hence the results are more accordant than those obtained by the chemical method first described in this paper.

During the course of our investigation there were two marked changes in the tare of our balloon. One of these has been described. The other arose from the circumstance that the thin paraffine (vaseline) which was most suitable for lubricating the stop-cocks during the winter no longer kept the joints tight when the heat of approaching summer rendered the material more liquid; and it became necessary to remove the stoppers and relubricate them, and it was the excess of cerate then used which melted and ran into the tubulatures subsequently.

There are then three separate values of the tare of the empty balloon to be used in our further calculations, all determined by or dependent upon Regnault's method, and all known with equal accuracy. These values we shall distinguish by the letters A, B, and C, and we shall designate by the same letters the experimental data or calculated results into which these values enter as elements.

Tare of Empty Balloon.

Values.	
A	2.5098 grams.
B	2.5573 "
C	2.5480 "

DENSITY OF AIR FREED FROM MOISTURE AND CARBONIC ACID.

In these determinations the balloon was placed in the calorimeter case and connected with the Bunsen pump through an overflow jar. Air was then drawn into it through the purifiers we have described, and the reflux current which followed for a moment when the inlet cock was closed was supplied from the previous overflow. In other respects the determinations were made as before described, and we obtained the following data for the weight of air held in the balloon at different temperatures and pressures.

Summary of Air Weights.

A No. 1, weight of air at 762.63 mm. and 18°.52 = 6.0347 grams.
A No. 2, " " 758.71 " " 19°.96 = 5.9745 "
B No. 1, " " 750.30 " " 23°.32 = 5.8411 "

Reducing now these weights to what they would have been at the temperatures and pressures we have assumed as standards, we obtain the following comparable values.

Reduced Air Weights for

H = 761.99 mm. = 300 d. in.* and
T = 27° C. = 300° absolute temperature.

A No. 1	5.8584 grams.
A No. 2	5.8588 "
B No. 1	5.8586 "
Average value	5.8586 grams.†

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* We shall use the abbreviation d. in. for tenths of an inch, after the analogy of d. m. for tenths of a meter.

† In the calculations of density and specific gravity, a still further, although wholly unimportant, correction has been made for the buoyancy of the air on the *brass* weights used to complete the tare in weighing the balloon, and in this connection it must be borne in mind that the *platinum* or *aluminum* fractions of a gram in a set of weights have always been adjusted to the larger *brass* weights in the air, and are therefore the equivalent of *brass* weights of the same denomi-

DENSITY OF HYDROGEN.

We have for the weight of hydrogen held by the balloon the following data.

B No. 1, weight of hydrogen at 763.10 mm. and 21°.08 = 0.4164 gr.
B No. 2, " " 764.92 " " 20°.52 = 0.4178 "
B No. 3, " " 758.96 " " 22°.75 = 0.4123 "

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nations. The volume of the counterpoise was adjusted when the balloon was full of air; but although the compensation may be perfect through all ordinary changes of temperature and pressure, it cannot be regarded as absolute. In a laboratory, such changes seldom amount in the aggregate to more than the equivalent of one twentieth of the normal atmospheric pressure; and although such a variation might not produce a sensible effect on the apparent weight of the small amount of brass used in our weighings, twenty times this effect, which we should have if the brass weights were wholly uncompensated, might be an appreciable quantity. In weighing the balloon the largest amount of brass weights used was about 11.5 grams, which at 300 d. in. and 27° C. displace 1.6 m.g. of air. One twentieth of this value would be barely, if at all, perceptible, but the whole quantity might cause a serious error in our results.

The tare of the empty balloon as first found by Regnault's method was 2.5573 grams; and we must assume that in the system consisting of balloon counterpoise and weights there may be outstanding a very small uncompensated volume, so that the true tare would be represented by

$$W_R = 2.5573 \pm w.$$

We next find the weight of the balloon filled with hydrogen gas, and it is obvious that under standard conditions the true weight, or

$$W' = 2.5573 \pm w + 0.4076 - w',$$

where w' represents the buoyancy of air on 0.4076 gram of brass. So the true weight of the balloon filled with air must be

$$W'' = 2.5573 \pm w + 5.8594 - w'',$$

where w'' represents the buoyancy of air on 5.8594 grams of brass. In like manner, the true weight of the balloon filled with carbonic acid gas is

$$W''' = 2.5573 \pm w + 8.9564 - w''',$$

where w''' is the buoyancy of air on 8.9564 grams of brass.

Taking 1.176 m.g. as the weight of 1 c.c. of air at 300 d. in. and 27° C., the standard conditions to which the weights have been reduced, we have

$$w' = 0.05 \text{ m. g.}, \qquad w'' = 0.84 \text{ m. g.}, \qquad w''' = 1.28 \text{ m. g.};$$

and further,

$W' - W_R = 0.4076 - 0\ 00005$ gram. True weight of hydrogen.
$W'' - W_R = 5.8594 - 0.00084$ " " " air:
$W''' - W_R = 8.9564 - 0.00128$ " " " carbonic acid.

These corrections should be applied to the weights before calculating the specific gravities, although they only alter the last values one or two units in

Reduced Weights.

H = 300 d. in.	T = 27° C.
B No. 1	0.4076
B No. 2	0.4072
B No. 3	0.4081
Average	0.4076

SPECIFIC GRAVITY OF HYDROGEN.

Air = 1.

The values were obtained by dividing each of the weights of hydrogen above given by the average weight of air (5.8586), after reduction for the temperatures and pressures at which the hydrogen weights were observed. The calculations were verified by dividing each of the reduced weights of hydrogen by the average reduced weight of air as above, and the same figures were obtained in both ways.

B No. 1	0.06957
B No. 2	0.06951
B No. 3	0.06966
Average	0.06958
Average using values of tare by chemical method	0.06962

SPECIFIC GRAVITY OF OXYGEN.

Hydrogen = 1.

In this investigation we have not made an additional determination of the specific gravity of oxygen gas referred to air, for the causes of error which are serious in the case of hydrogen are not appreciable when working with the heavier gas, and we cannot expect to improve

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the last decimal place; and in this paper, as is usual, the decimals are carried out one figure beyond the limits of accuracy.

In the chemical method we also took the weight of the balloon filled with carbonic acid gas, and, as before, we have

$$W''' = 2.5573 \pm w + 8.9564 - w'''.$$

Then by chemical means we determined the absolute weight (*in vacuo*) of the carbonic acid which the vessel held, that is, the quantity represented by $8.9564 - w'''$. Subtracting this value from the total weight, we obtained the tare of the empty balloon by the chemical method, and this obviously is

$$W_C = 2.5573 \pm w.$$

Thus, the buoyancy of the air on the weights is eliminated, and W_C is directly comparable in all its relations with W_R.

on the results of Regnault. Assuming, then, for the specific gravity of oxygen gas referred to air the value 1.10562, as obtained by Regnault and corrected by Crafts, and dividing this value by each of the values for the specific gravity of hydrogen gas given above, we have the following values for the specific gravity of oxygen referred to hydrogen.

B No. 1	15.892
B No. 2	15.907
B No. 3	15.873
Average	15.891
Average of chemical method	15.882
Value found by Lord Rayleigh	15.884

Density of Carbonic Acid.

For the weight of carbonic acid gas held in the balloon at different temperatures and pressures we have the following data.

B No. 1,	weight of CO_2 at	756.73	mm. and	22°.40	9.0334	gr.
C No. 1,	" "	760.50	" "	25°.56	8.9821	"
C No. 2,	" "	759.13	" "	26°.60	8.9348	"

Taking now the average value of the weight of air held in the balloon at 300 d. in. = 761.99 mm. and 27° (viz. 5.8586 grams), and reducing this weight to what it would have been under the condition at which each of the four weights just given was observed, and then dividing each of these weights (corrected as by previous note) by the weight of air under the same conditions, we obtain the following results.

Specific Gravity of Carbonic Acid. Air = 1.

	Wt. of CO_2.	Wt. of Air.	H	T	Sp. Gr.
B No. 1	9.0321	5.9088	756.73	22°.40	1.52858
C No. 1	8.9808	5.8753	760.50	25°.56	1.52855
C No. 2	8.9335	5.8445	759.13	26°.60	1.52855
	Average value				1.52856
	Average value by chemical process*				1.52854

Taking lastly the average value of the weight of hydrogen held in the balloon at 761.99 mm. and 27° (viz. 0.4076 gram), and dividing the several weights of carbonic acid by this weight reduced to the same conditions, we have, —

Specific Gravity of Carbonic Acid. Hydrogen = 1.

	Wt. of CO_2.	Wt. of H_2.	H	T	Sp. Gr.
B No. 1	9.0321	0.4111	756.73	22°.40	21.971
C No. 1	8.9808	0.4088	760.50	25°.56	21.971
C No. 2	8.9335	0.4066	759.13	26°.60	21.971
	Average value				21.971
	Average value by chemical process				21.957

The close agreement, indeed the essential identity, of these results should be noticed, as this fully substantiates the extreme accuracy of the method of recovering the lost tare of the empty balloon described on page 224. It is true that, as the values of the specific gravity of carbonic acid have been calculated with an average value of the several reduced weights of hydrogen or air, an error in these data would not affect the results; but any error in the observed weights of carbonic acid would appear to its full extent.

Moreover, the striking fact should not be overlooked that the specific gravity of carbonic acid gas referred to hydrogen approaches much more nearly 22, the half molecular weight of carbonic acid gas as generally assumed, than does that of oxygen gas when referred to the same standard, the corresponding whole number 16, and the significance of the circumstance is obvious. If we assume that the atomic weight of oxygen as determined by Dr. Richards under my direction is 15.87,* then the corresponding atomic weight of carbon would be 11.90, and the half molecular weight of carbonic acid 21.82. Theoretically, this number ought also to define the specific gravity of carbonic acid gas referred to hydrogen gas, if the two gases were compared under the same conditions of high temperature and indefinite expansion. But under the great pressure of our atmosphere the molecular volume of carbonic acid gas is known to be condensed to a measurably greater degree than the potentially equal molecular volume of hydrogen gas, and the result must be a proportionally increased density; and, moreover, the inequality in the condensation of the two gases must be increased by the circumstance that at the ordinary temperature of the air carbonic acid gas is below the critical point, while hydrogen gas is very far above it. If, however, this is true in the case of carbonic acid gas, our knowledge of the deviations from Mariotte's law compels us to infer that the same must be true in some small measure, although in a much less degree, in the case of oxygen gas;

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* These Proceedings, vol. xxiii. p. 185.

and it would lead us to expect that the specific gravity of oxygen gas referred to hydrogen gas would be slightly greater, certainly not less, than the corresponding half molecular weight. Now we have from the results published in this and our preceding paper, —

Half molecular weight of carbonic acid gas	21.82
Sp. Gr. of carbonic acid gas (referred to hydrogen gas) .	21.96

Half molecular or atomic weight of oxygen gas . . .	15.87
Sp. Gr. of oxygen gas (referred to hydrogen gas) . . .	15.88

It has been thought to discredit the low value of the atomic weight of oxygen we have found by the very easy but wholly gratuitous assumption that the hydrogen gas on which we experimented was impure, and we had intended in this investigation to demonstrate the identity of the gas from the several sources employed by a comparison of their specific gravities. We are under great obligations to Lord Rayleigh, who has relieved us from this necessity by anticipating the work. He has experimented on hydrogen gas, not only from all the sources we used, but also on gas which had been occluded by palladium, and has obtained the same result in all cases; namely, the value 15.884,* essentially identical with that which we have found in this investigation with the hydrogen gas from our electrolytic apparatus.†

This point, however, had not been overlooked in the previous paper. It was there shown that the results obtained, in *three distinct series of experiments*, with hydrogen gas prepared by *three different processes* and with *three different forms of apparatus*, were essentially identical.‡ On the doctrine of chances, such an agreement would have been practically impossible had there been an appreciable amount of accidental impurities, in the gas from either of the sources. We say accidental impurities, for there may be inherent impurities common to the gas from all sources, of which we as yet know nothing; and, as we wrote before, " The question still remains, Is the hydrogen gas thus prepared the typical hydrogen element? But this is the same question which must arise in regard to any one of the elementary substances; and all that we can say is, that the evidence in regard to the purity of the hydrogen we have used is as good as any that can be adduced in regard to any one of the elementary substances whose atomic weight has been most accurately determined." §

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* Proceedings of the Royal Society, vol. xlv. p. 425.

† These Proceedings, vol. xxiii. p. 168.

‡ See table, these Proceedings, vol. xxiii. p. 173.

§ These Proceedings, vol. xxiii. p. 174.

It is not to be expected that our results, or those of our contemporaries, are final. The most that has been accomplished by recent investigation is to show that the ratio of the atomic weight of oxygen to that of hydrogen, deduced from the elementary substances, as we know them in their purest condition, is decidedly less than that of 16 to 1. The evidence as to the exact value of this ratio is still conflicting, and although after our experience we cannot see how greater accuracy could be gained by any variation of our process, we are far from claiming that our results have not been vitiated by unknown constant errors. Fortunately, an exact knowledge of the ratio is at present of no practical importance in chemical analysis. The only question on which the actual small indefiniteness has a bearing is the unit of atomic weights, a question that has been much discussed of late; but here, as it seems to us, one consideration should be conclusive.

Every one who has worked on the oxygen and hydrogen ratio knows that the resources of experimental science have been taxed to the utmost in these investigations. Greater accuracy is not to be expected with our present appliances, and yet there is an outstanding uncertainty amounting to more than one half of one per cent of the value. This corresponds to a variation of more than one unit in many of the higher atomic weights; and unless we are willing that these *chemical constants* should fluctuate to this extent with every new determination of the fundamental ratio, we must seek a more invariable basis. The most natural and stable unit is the atomic weight of oxygen, not only on account of the wonderful combining power of this element, but also because the ratio of the combining weights of most of the elements to that of oxygen are known with great precision; and many cogent reasons could be urged for returning to the system of Berzelius, which referred all the other weights to that of oxygen, assumed to be 100. But this system would not exhibit to advantage the numerical ratios on which modern chemical classification is based. Hence for a provisional system we most warmly approve of that which assumes $O = 16$ as its basis, and of the best known atomic weights leaves only the value of H to vary with our changing knowledge. This system has all the stability it is possible at present to secure, and exhibits to advantage the relations which are important in classification. Moreover, it is no small recommendation to this system that a large number of the weights are whole numbers, within the limits of error of ordinary analytical work, and for this reason can be easily remembered.

In conclusion, I would express my obligations to my nephew, Dr.

PLATE I.

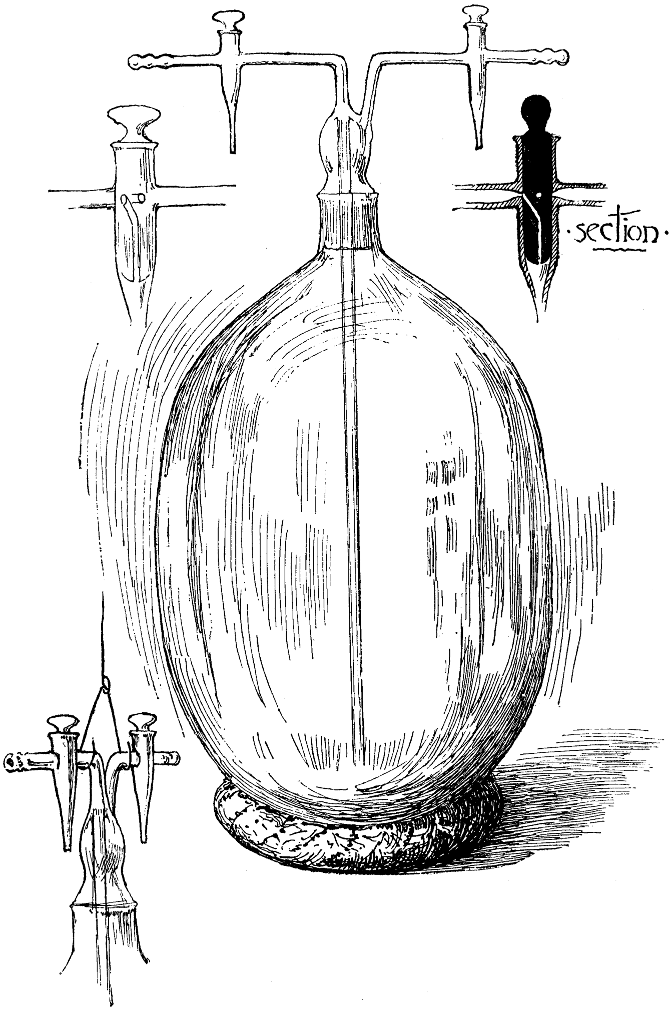


PLATE II.

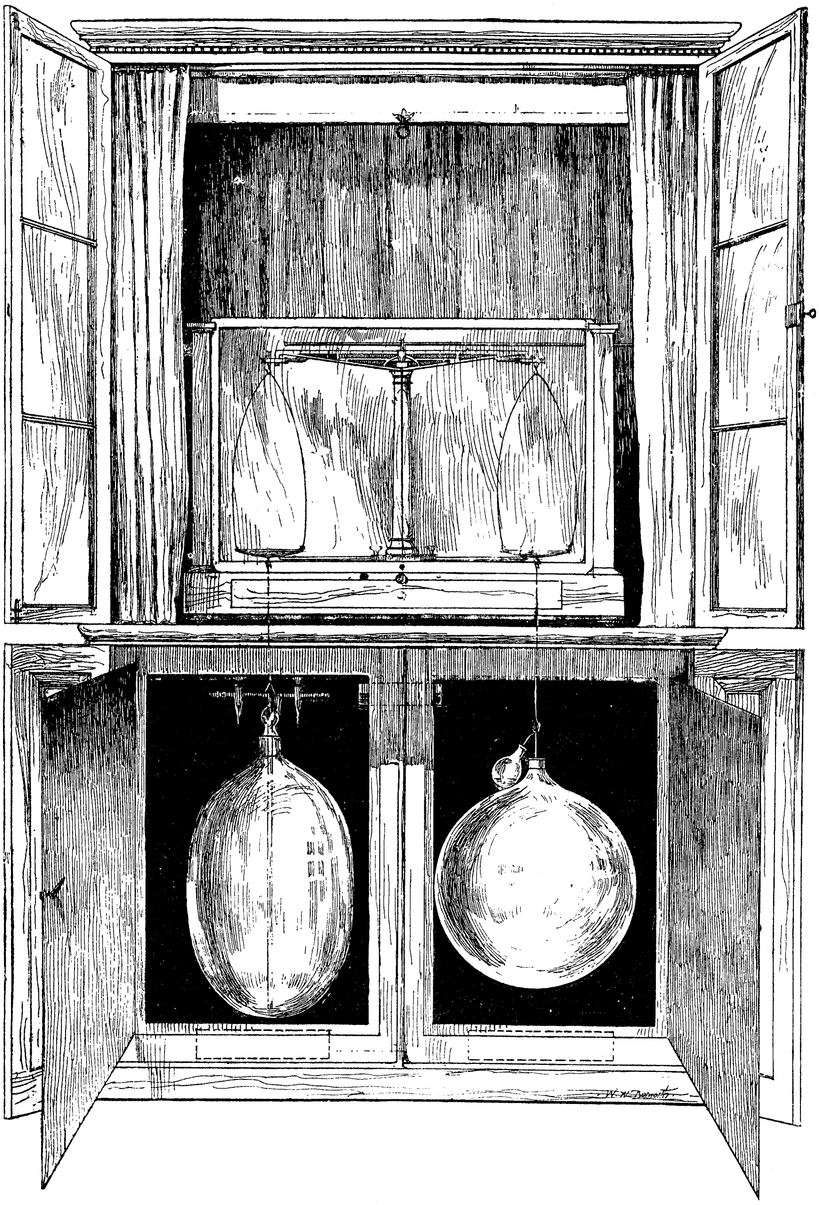
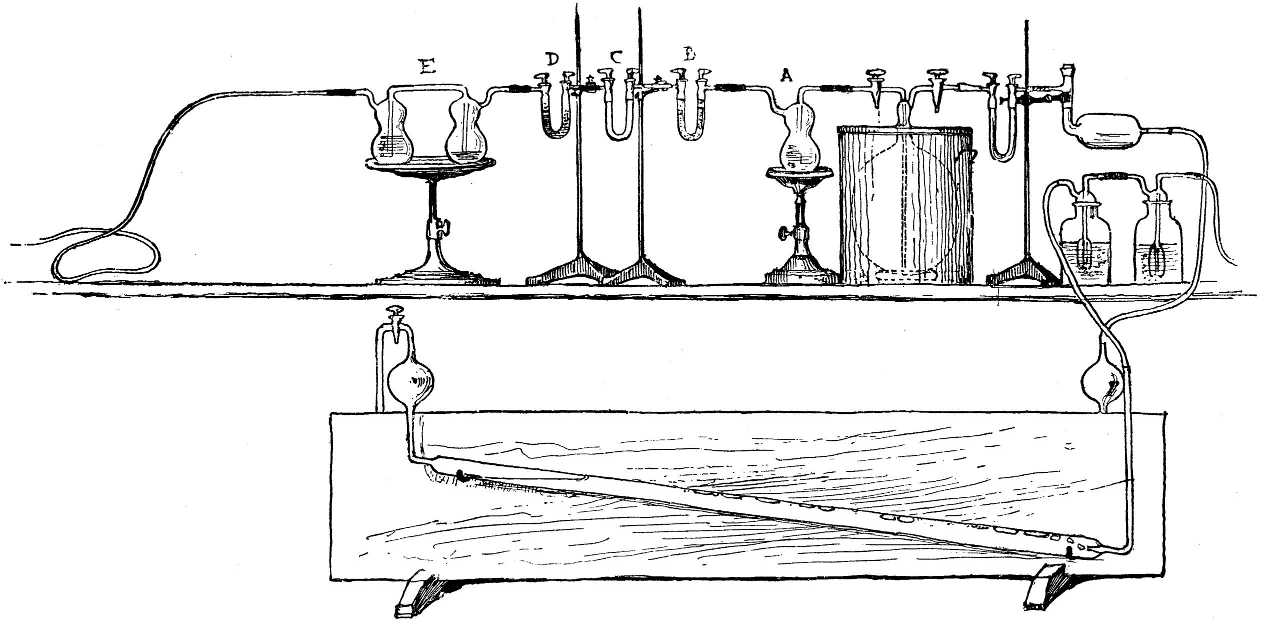


PLATE III.



Oliver W. Huntington, for the great aid he has given throughout this investigation. With the help of his skill in glass-blowing I have been able to secure all the connections of my gas generators with melted or cement joints, except the direct connections with the globe, where india-rubber could not be avoided. He has also constantly assisted my impaired eyesight in the observations with barometer and thermometer on which the accuracy of the work greatly depended. I have likewise been indebted to Dr. Arthur M. Comey for making the titrations required, and to Mr. W. W. Bosworth for the drawings with which this paper is illustrated.